

CHAPTER II

CHEMISORPTION THEORY

The theory of chemisorption has long remained a challenging theoretical problem¹². Our aim is only limited to study of hydrogen chemisorption. The theory of hydrogen chemisorption can be extended to describe all other complicated adsorbates.

2.1 The semi-empirical approach.

We shall consider neutral hydrogen molecules far from a clean metal surface. Approaching the surface, the molecules become dissociated. The resulting two atoms become so separate that they may be considered as having no interaction between each other. The atom is now adsorbed at a specific site on the surface. Let us first propose the interaction between atoms and metal surface to be of a chemical bond. There are three possibilities,^{2,10}

- i) $M. + .H \quad M : \bar{H}^+$, ionic bond,
- ii) $M. + .H \quad M^+ : H^-$, ionic bond,
- iii) $M. + .H \quad M:H$, covalent bond,

where the bonds in the first two are ionic and the third is neutral covalent. In the first case, the heat of adsorption is expressed as:

m

$$q = -\frac{1}{2}D(H-H) - eI + e\phi + e^2/4R, \quad (2.1.1)$$

where $D(\text{H-H})$ is the dissociation energy added to break the hydrogen molecule, eI is ionization energy added to remove the ground state electron of H-atom to infinity, $e\phi$ is the negative of work function (the energy we gain from the process of moving an electron from infinity to the metal surface then put into the lowest unoccupied level (Fermi level)), $e^2/4R$ is the classical image potential, the Coulomb interaction between the H-ion and metal surface, where R is approximated to be the ad-ion radius. Similarly for the second case we have

$$q = -\frac{1}{2}D(\text{H-H}) + eA - e\phi - e^2/4R, \quad (2.1.2)$$

where eA is the affinity energy we gain from the process of removing an electron from infinity and putting it into the lowest unoccupied level. This is not exact process for when we add an electron into the H-atom, the problem we obtain, is now two electron problem. All electronic levels are shifted because of two electron interaction. For hydrogen, we have $eI = 13.6 \text{ eV}$, $eA = 0.7 \text{ eV}$, $D(\text{H-H}) = 4.46 \text{ eV}$. As an example, if we choose W as adsorbent, we have $e\phi = 4.54 \text{ eV}$ and $R = 1.41 \text{ \AA}$, thus gives $e^2/4R = 2.25 \text{ eV}$. Thus we get $q = -9.04 \text{ eV/atom}$ or $-210 \text{ kcal/gm-atom}$ for the first ionic case and $q = -8.23 \text{ eV/atom}$ or $-115 \text{ kcal/gm-atom}$ for the second ionic case. This is too highly endothermic to occur spontaneously. Thus the ionic chemical bond fails to describe H-chemisorption, since it is an spontaneous process. Many gases adsorbate such N_2 , CO also give high endothermic heat of adsorption.

Let us apply the ionic model to alkaline metals adsorbate on transition metals such as W. The first case occurs because the alkaline metals have electronegativity less than that of W and hence tendency to loss electron will be higher. Thus



where $q = e\phi - eI + e^2/4R$. (2.1.3)

The results are shown in table 1.1.² , where N is Avogadro's number

Table 1.1²

		* N ϕ e	* N Ie	* Ne ² /4R%	# q _d (cal)	# q _d (exp)
Na	on W	104.0	118.0	44.5(1.83Å)	30.5	32.0
K	on W	104.0	99.6	35.9(2.27Å)	40.3	-
Ca	on W	104.0	89.4	31.1(2.62Å)	45.7	64.0

* in kilocalories

in kilocalories per gram atom

% in parentheses is R

The ionic model would be good for Na on W but not for Ca on W. This calculation may contain an error due to the rough estimation of R and the failure of classic theory for the short distance as 1-3 Å. However, this errors should not be large.

We will now consider the third type of bonding, covalent bond. This was first proposed by Eley (1950).^{13,14} He proposed the equation

$$q = D(\text{MH}) - \frac{1}{2}D(\text{HH}) , \quad (2.1.4)$$

where $D(\text{MH})$ and $D(\text{HH})$ is dissociation energy of metal surface-hydrogen bond and hydrogen molecule. He assumes that no metal-metal bond is broken upon chemisorption. This is however not always true. To determine $D(\text{MH})$, Eley used the Pauling's approximation¹⁵

$$D(\text{MH}) = (D(\text{MM}) + D(\text{HH}))/2 + 23.06(X_M^P - X_H^P)^2 , \quad (2.1.5)$$

where X_M^P and X_H^P is electronegativity defined by Pauling.

Applying this to 2.1.4, we get

$$q = \frac{1}{2}D(\text{MM}) + 23.06(X_M^P - X_H^P)^2 . \quad (2.1.6)$$

$D(\text{MM})$ is estimated from latent heat of sublimation, λ . In FCC metal, each metal atom has 12 nearest neighbours, and each bond has two metal atom, so that

$$D(\text{MM}) \approx \lambda/6 . \quad (2.1.7)$$

Stevenson (1955)¹⁶ has made use of Mulliken's electronegativity values defined by

$$X^M = \frac{1}{2}(I_e + \Lambda_e) . \quad (2.1.8)$$

For metals, both eI and $e\Lambda$ are equal to the same value $e\phi$, the work function of the metals, since the highest occupied and lowest unoccupied level are at the Fermi level,

Stevenson's modification gives us a better value of $D(MH)$ when compared to experiments. Neither the origin Eley's method nor its modification gives completely satisfactory agreement with experiment value. For hydrogen on Fe, Co, Ni, Cu, Mo, Ta and W, the agreement using Stevenson's procedure is moderately good: the values for Pd and Pt are rather low; the value for Cr is very low while the values for Ru, Rh and Ir are too high. In general, the values for other gases are low (this was shown by Bond 1962).¹⁷

Both Eley and Stevenson did not take into account of the surface effects. Ehrilich (1959)¹⁸ point out that Eley missed two important points. The first is that the estimation of $D(MH)$ from latent heat of sublimation is too high. This point was indicated in Oriani's work (1950)¹⁹ on the surface excess energy (the energy to bring an atom from interior to the surface) for liquid metals. The excess energy calculated from the heat of evaporation assuming pairwise bonding was shown to be high when compared to the values calculated from surface tension measurements and their temperature coefficients. The bonds in the surface layer were found to be about 13-25% stronger than in the bulk. The second point is that the geometric mean is better than arithmetic mean to estimate $D(MH)$. This idea came from Pauling's work on metal hydrid.¹⁵ Ehrilich has investigated the result of modification on the series of transition metals. He found the poor agreement for all transition metals, though chemisorption of hydrogen on Zn, Cd and Hg were correctly predicted to be endothermic adsorption.

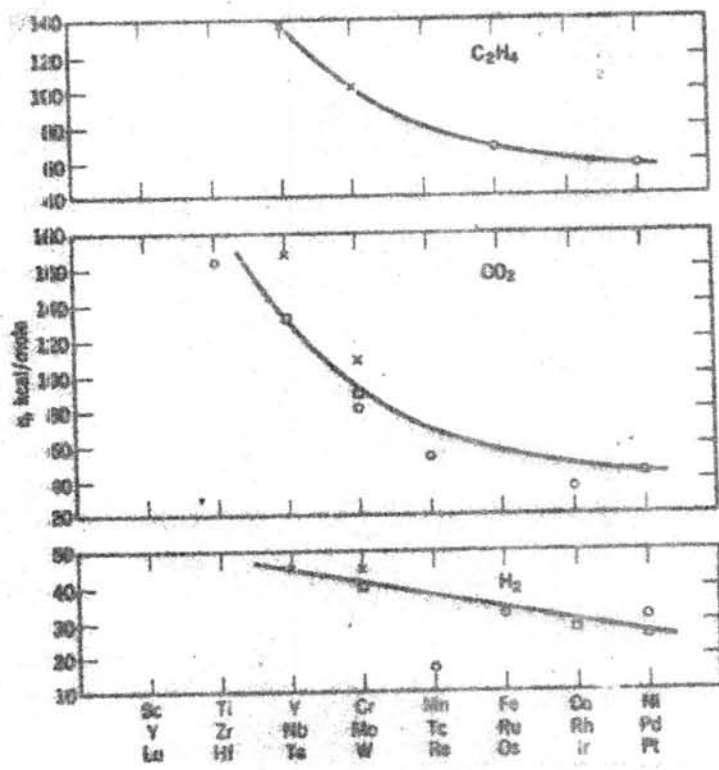


Fig. 2.1.1 : Heat of chemisorption for the transition metals, plotted according to periodic classification. and denote first, second, and third periods, respectively.

Before we go further, let us look at the correlation of some gases chemisorption on transition metals series, show in Fig 2.1.1.³ We see that there exist a general rule to govern the behavior of gases chemisorption on transition metals.

Neither Eley's method nor its modification can give results which can explain even qualitatively the sequence of heat of adsorption variation on transition metals series.

Higuchi et.al. (1957),²⁰ using a simple quantum mechanical approach based on a proposal of Wall (1939),²¹ have calculated the percentage of the ionic character of covalent adsorption bonds and heat of adsorption. The surface complex is approximated to be M-H. They start

$$\Psi = c_i \cdot \Psi_i + c_c \cdot \Psi_c \quad , \quad (2.1.9)$$

where Ψ_i and Ψ_c are eigenfunctions of ideal ionic and covalent bond respectively, c_i and c_c are constants.

Substituting 2.1.9 into

$$E = \frac{\int dr. \Psi^* \cdot H \cdot \Psi}{\int dr. \Psi^* \cdot \Psi} \quad ,$$

thus they get
$$E = c_i^2 \cdot H_{ii} + c_c^2 \cdot H_{cc} \quad , \quad (2.1.10)$$

where $c_i^2 + c_c^2 = 1$. Rearranging the terms, 2.1.10 becomes

$$c_i^{-2} = 1 + (E - H_{ii}) / (E - H_{cc}) \quad . \quad (2.1.11)$$

By setting
$$H_{ii} = A_M e - I_e + \frac{8}{9} \cdot (e^2/R) \quad (2.1.12.a)$$

and
$$H_{cc} = \frac{1}{2}(D(MM) + D(HH)) \quad , \quad (2.1.12.b)$$

where $A_M e$ is electron affinity of metal M. They calculated c_i^2 from the expression

$$\mu = c_i^2 \cdot eR \quad , \quad (2.1.13)$$

where μ is the bond moment (which was discussed and measured by Mignolet (1950))²². Thus Higuchi et.al. were able to obtain some information about the nature of the bonds.

The result of Higuchi et.al. shows that the bonds for Cs and Na on W are purely ionic while the bonds for Ba and Sr on W are ionic with a small amount of covalent character ($c_i^2 = 0.97$ for Ba and 0.67 for Sr.). For gases on metals the bond are covalent with a small amount of ionic character ($c_i^2 = 0.02$ to 0.09). For strongly covalent bonds, they find bond energy which differ only a little from those obtained by Eley. Thus we find that Higuchi's method fails to explain the gases chemisorption on transition metals series.

All the semi-empirical theories, which have been discussed, fail to show the nature of the chemisorption bond of an adsorbate on a transition metal surface.

2.2 The recent chemisorption theory.

The chemisorption theory, recently developed, can be divided into two main approaches the molecular and solid states approaches. The molecular approach uses conventional quantum chemistry methods, e.g. Extended Hückel theory (EHT) methods,²³⁻²⁷ and its modification,²⁸ Complete Neglect Differential Overlap (CNDO) methods,^{29,30} SCF-X α Scattered-Wave methods,³¹⁻³³ to calculate a finite cluster of metal and adatoms, the chemical complex $M_n A$. The number n involved is usually of order 10 only, which is far from being a real crystal. It is limited by the power of computer. The solid states approach requires two limits to be considered, the tightly bound and nearly free electron models.

In analogy to the conventional molecular theory, the tightly bound model can be approached in two principle ways, the Hartree-Fock (HF or MO)scheme and Heitler-London (HL or VB) scheme. The former approach was first developed as a simple one electron approximation, (see Koutecky (1958)³⁴, Grimley (1957, 1958)^{35,36}) Newns (1969)³⁷ showed the short coming of the simple one electron approximation and suggested that the problem could be approached by using the Anderson (1961)³⁸ model. In this approach, the electron correlation is added and shown to play an important role (see also chapter IV and V). Schrieffer and Gomer (1971)³⁹ introduced a new extreme approach, the Induced Covalent Bond (ICB) theorem which is a generalized of conventional HL or VB theorem. The ICB theory was developed

further by Schrieffer and Paulson (1975).⁴⁰ The basic idea of this theory is that the adatom electron-electron interaction is so large that the electron fluctuation can be considered to be zero and the solid is considered as being analogous to an atom in the HL or VB theory.

In nearly free electron model, the metal is assumed to be semi-infinite jellium. The problem of jellium electronic structure is solved by the use of Density Functional Formalism, which was developed by Hohenberg, Kohn and Sham (1964-1966).⁴¹⁻⁴⁵ The adatom, e.g. hydrogen has its valence electron removed and placed in the jellium. Then, slowly the proton is moved to the surface. The $N + 1$ electrons in the jellium become perturbed and thus redistribute themselves. This is the basic idea that Smith, Ying and Kohn (1973),⁴⁶ Lang and Willium (1975-1977),⁴⁷⁻⁴⁹ Gunnarsson, Hjelmsberg and Lundquist (1976)⁵⁰ etc., have used to discuss the chemisorption on simple metals. Muscat and News (1977)⁵¹ discussed the relation of the level shift in News-Anderson model to the chemisorption on jellium with the use of this formalism.

The central to these theories is News-Anderson model. We should note that the one electron theory is the limiting case for the zero adatom electron-electron interaction; the conventional quantum chemistry approach is the limiting case for the adatom-metal atoms, at surface, coupling potential is large; the ICB method is the limiting case for infinite electron-electron interaction; while the chemisorption on jellium is the limiting case for large band width metals.

2.3 Newns-Anderson model.^{11,37,38,52-54}

The adsorption phenomena can be related to the impurity problem since the adsorbate atom can be considered to be a surface impurity. Newns (1967, 1969)^{37,55} and Grimley (1967)^{56,57} have used Anderson model for studying localized magnetic moment in metals to study the chemisorption phenomena. This model is very successful in both fields, and thus can be considered to be a general one. In Newns' (1969)³⁷ paper, many physical interpretation and beautiful argument on the chemisorption phenomena were discussed, e.g. the surface molecule concept. This concept provides the reasons for working on chemisorption problem with the usual quantum chemistry methods. The generalized chemical bond was taken to be made up of $N + 1$ electron chemical bond.¹¹ The classical electron pair chemical bond concept is just the special case, i.e. $N = 1$, of the generalized chemical bond. This generalized chemical bond needs further theoretical development and will not be discussed in this thesis.

There are significant changes, due to the surface effect, in the parameters ϵ_k , ϵ_l , U , V_{lk} in Anderson Hamiltonian and also the density of states $\rho_0(\epsilon_k)$ of metal. The surface effect is important even in the ideal unperturbed metal surface, which will be discussed in detail in chapter III. While we can use the bulk ϵ_k and ρ_0 , the wave function and the local density distribution can not be used. When the adsorbate comes near the surface, the ionization energy eI and affinity energy eA would be screened by metal surface charge,^{52,58,59} i.e.

$$\epsilon_{\ell} = eI = I_0 + V_{im}$$

and

$$eA = A_0 - V_{im}$$

thus

$$U = eA - eI = U_0 - 2V_{im} ,$$

where V_{im} is expressed classically as $e^2/4d$. The change can be significantly large at the ideal metal surface. Unlike the impurity problem the covalent admixing matrix element $V_{\ell k}$ can not easily be expressed as mean average or root mean square average.